Express Mail No.
EQ 330858325 US
10/551606

Patent Applic **C20 Rec'd PCT/PTO 3 0 SEP 2005**

SYNTHETIC ZEOLITE, IN PARTICULAR FOR CATALYTIC
HYDROISOMERIZATION OF HIGHER PARAFFINS

The invention relates to a zeolite of the ZSM-12 type, to a catalyst which is suitable in particular for the hydro-isomerization of higher paraffins, to a process for produc-ing such a zeolite of the ZSM-12 type or such a catalyst, and to the use of the catalyst.

The isomerization of paraffins is one of the most important refinery processes. Very recent legal restrictions in the use of aromatics and methyl tert-butyl ether in automotive gasoline are making the isomerization of higher paraffins (greater than C_5) in particular one of the most important alternatives for increasing the octane number in automotive gasoline. This is especially true of the isomerization of C_8 paraffins.

To date, it has not been possible to carry out such isomerizations owing to the excessively low selectivity, i.e. owing to the formation of large amounts of cracking products.

In recent times, a series of investigations of the use of zeolites as catalysts for hydroisomerization and hydro-cracking of higher paraffins have been carried out. For instance, W. Zhang and P.G. Smirniotis (J. Catal. **182,** 400-416 (1999)) report on the influence of the zeolite struc-ture and its acidity on the selectivity and the reaction mechanism for the hydroisomerization and the hydrocracking of n-octane. The catalysts investigated were ZSM-12, USY and β-zeolites with varying Si/Al ratios. In the synthesis of the ZSM-12 zeolites, aluminum is removed from the zeolite by dealumination with hydrochloric acid in order to establish a certain Si/Al ratio. The thus produced zeolites

were investigated for their surface acidity and their catalytic activity. At temperatures of more than 290°C, n-octane is converted at conversion rates of about 50% with selectivities of from 27 to 41% to isooctanes.

A. Katovic and G. Giordano (Chemistry Express, Vol. 6, No. 12, 969-972 (1991)) describe the synthesis of ZSM-12 zeolites from the following hydrogel system: x Na_2O : y TEABr : z Al_2O_3 : 50 SiO_2 : 1000 H_2O (where 2.5 < x < 7.5; 3.5 < y < 10 and 0 < z < 1). In the preparation of ZSM-12 using precipitated silica, an Na_2O/SiO_2 ratio = 0.1, a TEABr/SiO_2 ratio = 0.2 and an SiO_2/Al_2O_3 ratio = 100 were used. In order to obtain pure crystalline (Na-TEA)-ZSM-12, the following conditions are recommended: Si/Al in the region of 50, OH^-/TEA^+ in the region of 1 and H_2O/OH^- in the region of 100.

US 5,800,801 describes an MTW zeolite, a process for its production and its use in the cracking of hydrocarbons. The MTW zeolite is also referred to as ZSM-12 zeolite. The zeolite has a certain x-ray diffraction pattern, and also a specific surface area of more than 300 m^2/g. For the production of the MTW zeolite catalyst, an aqueous solution of sodium silicate is prepared, to which a solution of tetraethylammonium hydroxide and an aqueous solution of aluminum nitrate are added, the amounts of the individual components being selected such that: SiO_2/Al_2O_3: > 120; TEA^+/SiO_2: 0.2 - 0.95; H_2O/SiO_2: 20 - 300; OH^-/SiO_2: 0.4 - 0.7.

US 3,970,544 and DE 22 13 109 C2 describe ZSM-12 zeolites, processes for their preparation and their use for converting hydrocarbons. The SiO_2/Al_2O_3 ratio in the ZSM-12 zeolites described is between 49 and 300. In the examples, the silicon source used is colloidal silicon oxide.

In the hydroisomerization of higher paraffins, large

amounts of low molecular weight cracking products are formed. These side reactions are generally promoted by high temperatures, which are required in order to achieve industrially sufficient conversion rates.

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It is therefore an object of the present invention to provide a zeolite of the ZSM-12 type which is suitable especially for use in a catalyst as is used, for instance, for the hydroisomerization of higher paraffins. It is a
10   further object of the present invention to provide a catalyst which leads to higher yields of isoparaffins especially in the hydroisomerization of higher paraffins, and also affords advantageous results in other conversions of hydrocarbons.

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This object is achieved with a zeolite of the ZSM-12 type as claimed in claim 1. Advantageous developments of the zeolite of the ZSM-12 type are the subject matter of the dependent claims. Furthermore, the invention provides a
20   catalyst which comprises the inventive zeolite of the ZSM-12 type. Further developments of this catalyst are the subject matter of the claims dependent upon claim 8.

It has been found that, surprisingly, when a combination of
25   certain features in the synthesis is complied with, particularly advantageous zeolites can be obtained, which are suitable, for example, especially for use in catalysts for the hydroisomerization of higher paraffins with high activity and good conversion, and it is possible to carry
30   out the reaction even at comparatively low temperatures.

The invention therefore first provides a zeolite of the ZSM-12 type, especially for use in catalysts for the hydro-isomerization of higher paraffins, which
35   (a)   has a primary crystal size of ≤ 0.1 µm;
            (b)   a specific volume, determined by mercury porosi-
                  metry at a maximum pressure of 4000 bar, of 30-

200 mm^3/g in a pore radius range of 4-10 nm; and which has further been

(c)   prepared from a synthesis gel composition comprising

c1)   an aluminum source

c2)   precipitated silica as a silicon source

c3)   TEA$^+$ as a template

c4)   an alkali metal and/or alkaline earth metal ion source M having the valency n;

c5)   in which the molar $H_2O:SiO_2$ ratio is selected between 5 and 18.

The inventive zeolite of the ZSM-12 type features a particularly high porosity. This is manifested clearly in the specific pore volume determined by mercury porosimetry, especially when it is placed in relation to the pore radius. In mercury porosimetry, the inventive zeolite of the ZSM-12 type exhibits, in a pore radius range of 4-10 nm, a specific volume of from about 30 to 200 mm^3/g, preferably about 80-150 mm^3/g, especially preferably about 100-130 mm^3/g. ZSM-12 zeolites which have been produced using colloidal silica have a distinctly smaller specific pore volume in this pore radius range. Typical values for a pore radius range of 4-10 nm are in the region of about 3 mm^3/g. In a pore radius range of 10-100 nm, the inventive zeolite of the ZSM-12 type has a specific pore volume of about 70-700 mm^3/g, preferably about 150-550 mm^3/g, especially preferably about 200-500 mm^3/g. A zeolite of the ZSM-12 type produced using colloidal silica exhibits, in the pore radius range of 10-100 nm, typically a specific pore volume of about 40 mm^3/g. The pore volume is determined by mercury porosimetry to DIN 66133 at a maximum pressure of 4000 bar (cf. Example 11). The aforementioned porosimetry values are determined on the zeolites which have been washed, dried and calcined according to Example 1. The above ranges for the specific volume also apply to the washed and dried but uncalcined zeolites.

The inventive zeolite of the ZSM-12 type has a high propor-
tion of large pores, as obtainable only in the inventive
composition according to claim 1. The inventive zeolite of
the ZSM-12 type exhibits, in nitrogen porosimetry in the
range of 30-200 Å, a specific volume of 0.05-0.40 cm^3/g,
preferably 0.10-0.35 cm^3/g, especially preferably 0.15-0.30
cm^3/g. It is assumed, without the invention being restric-
ted to this assumption, that the above porosimetry of the
inventive zeolite is also responsible for the high cataly-
tic activity and reflects the numerous cavities between the
small primary crystals. The specific pore volume is
determined by nitrogen porosimetry according to DIN 661134
as specified in Example 12. The above porosimetry values
may be determined on the dried uncalcined zeolites or
preferably on the calcined zeolites. The above porosimetry
values are determined on zeolites which have been washed,
dried and calcined according to Example 1. The above ranges
for the specific volume also apply to the washed and dried
but uncalcined zeolites.

It has been found that it is particularly advantageous when
the zeolite is synthesized directly with the desired
SiO_2/Al_2O_3 ratio by appropriately adjusting the amount of
silicon source and aluminum source in the primary synthesis
of the zeolite (in the synthesis gel composition). The
SiO_2/Al_2O_3 ratio in the synthesis gel composition corres-
ponds approximately to the SiO_2/Al_2O_3 ratio in the ZSM-12
zeolite. The SiO_2 fraction in the synthesis gel composition
deviates, in a manner familiar to those skilled in the art,
generally by about ± 10% from the fraction in the finished
zeolite. Only in the event of very large or very small
fractions of SiO_2 are larger deviations observed. As a
result, no subsequent dealumination of the zeolite to
adjust the SiO_2/Al_2O_3 ratio is required. The aluminum
content of the zeolite of the ZSM-12 type thus does not
subsequently have to be lowered by addition of acid and

leaching of aluminum atoms. It is assumed that the inventive direct synthesis enables a homogeneous structure of the zeolite and prevents what is known as "extra-framework" aluminum, which is formed in the subsequent dealumination after the zeolite synthesis, and can disadvantageously influence the activity and selectivity of the ZSM-12 zeolite.

It has been found that, surprisingly, the inventive advantageous properties of the zeolite can be realized when the synthesis gel used to produce the zeolite fulfills certain requirements. For instance, TEA^+ cations are used in accordance with the invention as a template (TEA = tetraethylammonium). Compared to this, $MTEA^+$ is unsuitable (MTEA = methyltriethylammonium). Particular preference is given to using TEAOH as a template. In principle, it is, however, possible to use any starting materials which supply tetraethylammonium ions. For example, TEABr may also be used.

The molar TEA^+/SiO_2 ratio established in the synthesis gel is preferably selected at a low level. The molar TEA^+/SiO_2 ratio is preferably selected between about 0.10 and 0.18. In the synthesis gel composition, the molar SiO_2/Al_2O_3 ratio is preferably established within the range of from about 50 to about 150.

The synthesis gel should preferably also have a comparatively low alkali metal and/or alkaline earth metal content, and the molar $M_{2/n}O:SiO_2$ ratio may advantageously lie between about 0.01 and 0.045. $M_{2/n}O$ is the oxide of the alkali metal or alkaline earth metal having the valency n. In addition, in accordance with the invention, a comparatively low molar ratio of $H_2O:SiO_2$ of from about 5 to 18, preferably from 5 to 13, in the synthesis gel is used. The metal ion M selected is preferably an alkali metal, especially preferably sodium.

Surprisingly, a considerable influence of the silicon source on the morphology and catalytic activity of the resulting ZSM-12 zeolite was found. For instance, in accordance with the invention, a precipitated silica is used which, in comparison to colloidal silica, has a lower reactivity. This also allows the mean size of the resulting primary crystals, which should be less than 0.1 µm in accordance with the invention, to be influenced. The precipitated silica preferably has a BET surface area of ≤ 200 m^2/g.

It is important that the average size of the primary crystals in the inventive catalyst is comparatively low and is less than 0.1 µm. The primary crystal size may be determined from scanning electron micrographs, by analyzing a number of primary crystals with regard to length and width. The measured primary crystal sizes are then used to form the arithmetic mean. The primary crystals present in the inventive catalyst generally do not have any significant differences in their lateral elongation in comparison to their longitudinal elongation. Should this occur in the individual case, the largest and the smallest diameter of the crystal are averaged in the determination of the primary crystal size.

Specifically, the procedure is to produce scanning electron micrographs of the washed and dried (cf. Example 1) but uncalcined, template-containing ZSM-12 zeolite at a magnification of from 68 000 to 97 676 (instrument: Leo 1530; LEO GmbH, Oberkochen, Germany). On the micrographs, 30 primary crystals are selected which are clearly delimited from one another, and their longitudinal and lateral elongation is measured (cf. above) and the mean is determined therefrom. The diameters determined in this way are then used to form the arithmetic mean, i.e. the mean primary crystal size. The primary crystal size is substan-

tially not influenced by calcining. The primary crystal
size can therefore be determined directly after the
synthesis of the zeolite of the ZSM-12 type, and also after
the calcination.

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The primary crystals preferably have a size in the range of
from about 10 to 80 nm, more preferably in the range of
from about 20 to 60 nm. The inventive catalyst thus
comprises comparatively small primary crystals.

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In a particularly preferred inventive embodiment, the
primary crystals of the zeolite are combined at least
partly to agglomerates. Advantageously, the primary crys-
tals have been combined to agglomerates in a proportion of

15   at least 30%, preferably at least 60%, especially prefer-
ably at least 90%. The percentage data are based on the
total number of primary crystals.

When the above-described conditions and features are

20   complied with in the synthesis of the inventive zeolite of
the ZSM-12 type, an apparently particularly advantageous
morphology of the agglomerates of the very small primary
crystals is surprisingly obtained, which also positively
influences the catalytic activity of the ZSM-12 zeolite.

25   Afterward, the agglomerates preferably have a large number
of cavities on their surface and interstices between the
individual primary crystals. The agglomerates thus form a
loose structure composed of primary crystals with cavities
accessible from the agglomerate surface or interstices

30   between the primary crystals. On scanning electron micro-
graphs, the agglomerates appear as a sponge-like structure
with a highly fissured surface which is generated by the
loose coherence of the primary crystals. The micrographs
preferably show relatively large spherical agglomerates

35   which have a broccoli-like shape. The structured surface is
formed from primary crystals which form a loose structure.
Between individual crystals, cavities are formed, from

which channels lead to the surface, which appear on the micrographs as darkly contrasted points on the surface. Overall, a porous structure is obtained. The agglomerates formed from primary crystals are preferably in turn joined to form larger, superordinate agglomerates, between which individual channels with larger diameter are formed.

In contrast, conventional zeolites of the ZSM-12 type exhibit, in scanning electron micrographs, a comparatively less structured and apparently smoother surface of the agglomerates. This is probably caused by the substantially lower porosity of the zeolite.

The inventive zeolite of the ZSM-12 type thus preferably forms an open agglomerate structure, i.e. a structure in which the primary crystals are not combined in such an ordered way that a substantially smooth or continuous surface of the agglomerates is obtained. Instead, the primary crystals form bridges between adjacent primary crystals, so that cavities are formed between adjacent primary crystals.

It is assumed, without any intention that the invention be restricted by this theory, that the particular agglomerate structure enables efficient access of the molecules to be converted to the active sites of the inventive catalyst and rapid transport of the converted molecules away from the active sites, and also particularly advantageous utilization of the catalytic activity even in the interior of the primary crystal agglomerates. For example, the high catalytic activity of the inventive catalysts in the hydro-isomerization of paraffins is influenced by the efficient diffusion of the paraffins to the active sites in the primary crystal agglomerates, as a result of which the reaction kinetics and thus also the yield of branched hydrocarbons can be improved. This enables the hydroiso-merization to proceed even at comparatively low tempera-

tures with good conversion rates and substantially without
side reactions which lead to the degradation of the carbon
skeleton to form low molecular weight hydrocarbons.

5   The primary crystals of the inventive zeolite of the ZSM-12
type are thus preferably combined to agglomerates, the size
of these agglomerates being highly variable, and it is also
possible for a plurality of agglomerates to be combined to
larger, superordinate agglomerates. In this case, the
10   primary crystals are predominantly recognizable by scanning
electron microscopy as delimited units, but are on the
other hand joined over part of their surface with adjacent
primary crystals to form agglomerates. Scanning electron
micrographs reveal relatively large, broccoli-like struc-
15   tures with a highly structured surface, which have combined
to larger, superordinate agglomerates. This structure is
not significantly impaired or altered by the processing of
the zeolite to the finished catalyst, especially by the
calcining, comminution, etc.
20
In a preferred embodiment, the number of the primary
crystals not bonded into agglomerates is minimized in the
inventive zeolite of the ZSM-12 type. Agglomerates are
understood to mean combinations of a plurality of primary
25   crystals.

The inventive zeolite of the ZSM-12 type exhibits a high
catalytic activity, especially in the hydroisomerization of
higher paraffins. The invention therefore also provides a
30   catalyst, especially for the hydroisomerization of higher
paraffins, comprising a zeolite of the ZSM-12 type as des-
cribed above. According to the invention, higher paraffins
are understood to mean those having at least 5 carbon
atoms.
35
In its simplest embodiment, the catalyst comprises only the
inventive zeolite of the ZSM-12 type. To this end, the

powder obtained in the preparation of the zeolite of the
ZSM-12 type, which may also initially be further ground and
adjusted to a certain particle size distribution, is, for
example, pressed to moldings without binders.

However, the catalysts may additionally also comprise
further components. For instance, the catalyst may comprise
further meso- and/or microporous materials. Meso- and
microporous materials are understood, for example, to mean
molecular sieves, especially aluminophosphates, metallo-
aluminates, titanosilicates and metallosilicates, for
example zeolites. The proportion of the meso- and/or micro-
porous materials may be between 1 and 99% by weight based
on the weight of the catalyst.

In a further inventive embodiment, the catalyst may be
processed to moldings with the aid of a binder. In
particular, the catalyst may have a binder content of from
about 10 to 90% by weight, preferably from 20 to 70% by
weight. The binder used may be any binder which is familiar
to those skilled in the art and appears to be suitable,
especially silicate materials, aluminum oxide, zirconium
compounds, titanium oxide, and mixtures thereof, and
materials, for example cement, clay, silica/alumina. Pre-
ferred binders include pseudoboehmite and also silicatic
binders such as colloidal silicon oxide.

The inventive catalyst is suitable generally, but not
exclusively, for conversion reactions of hydrocarbons. The
properties of the catalyst may be modified by covering the
catalyst with catalytically active components which influ-
ence its catalytic properties or which are themselves
catalytically active. Suitable for this purpose are, for
example, metals of the transition groups, particular
preference being given here to the noble metals. Suitable
examples are gold, silver, rhenium, ruthenium, rhodium,
palladium, osmium, iridium and platinum, and mixtures and

alloys thereof. Particular preference is given to platinum.

The catalytically active component is generally present in
the catalyst in a proportion of from 0.01 to 40% by weight
5   based on the total face of the catalyst. When the cataly-
tically active component used is a noble metal, it is
preferably present in the catalyst in a proportion of from
0.05 to 2% by weight.

10   The particular properties of the inventive catalyst are
influenced significantly by the preparation of the
catalyst, such as the composition of the synthesis gel, and
also the use of precipitated silica. The invention there-
fore also provides a process for producing the above-
15   described catalyst.

In the process according to the invention, a synthesis gel
composition is produced which comprises, in aqueous
solution or suspension:
20   a1)   an aluminum source;
            a2)   precipitated silica as a silicon source;
            a3)   TEA$^+$ as a template;
            a4)   an alkali metal and/or alkaline earth metal ion
                  source M having the valency n; and
25   a5)   the molar $H_2O:SiO_2$ ratio is set within the range
                  from 5 to 15;
the synthesis gel composition is crystallized under
hydrothermal conditions so as to obtain a solid. The solid
is removed, and optionally washed, dried and calcined.
30

The solid obtained in the process according to the
invention corresponds to the above-described zeolite of the
ZSM-12 type. It has primary crystals having a mean primary
crystal size of < 0.1 nm and exhibits, depending on the
35   pore volume, the above-described distribution, determined
by mercury porosimetry, of the specific pore volume.

As already explained in connection with the inventive
zeolite of the ZSM-12 type and the catalyst, the silicon
source used in the process according to the invention is
precipitated silica and the template used is tetraethyl-
5   ammonium ions.

In relation to the aluminum source, there are no particular
restrictions, so that it is possible in accordance with the
invention to use all customary aluminum sources familiar to
10   those skilled in the art. Suitable examples are activated
alumina, γ-alumina, aluminum hydroxide, sodium aluminate,
aluminum nitrate, or else aluminum sulfate. Particular
preference is given to sodium aluminate, since it functions
simultaneously as a source of alkali metal ions.
15

The alkali metal ion and/or alkaline earth metal ion source
used may be any customary compounds familiar to those
skilled in the art. The alkali metal used with particular
preference is sodium. The alkali metal sources used are in
20   particular alkali metal hydroxides, preferably sodium
hydroxide.

The procedure in the synthesis is preferably to initially
prepare a solution of tetraethylammonium hydroxide in
25   demineralized water. Subsequently, the aluminum source, for
example sodium aluminate, and also a source of alkali metal
and/or alkaline earth metal ions M having the valency n,
for example sodium hydroxide, is added to this solution,
and the mixture is stirred until a solution of the
30   constituents is obtained. Subsequently, the precipitated
silica is added in portions to this solution to obtain a
highly viscous gel. The synthesis of the zeolite is
preferably carried out in a small amount of water as a
solvent. To this end, the molar $H_2O:SiO_2$ ratio is adjusted
35   within the range from 5 to 15.

The molar ratio of the silicon and aluminum sources in the

synthesis gel composition corresponds substantially to the molar composition of the zeolite of the ZSM-12 type to be produced. In order to be able to take account of devi-ations, caused by the reaction kinetics, between the

5   composition of the synthesis gel and the desired composi-tion of the zeolite, it is possible optionally to carry out preliminary experiments to determine the suitable synthesis gel composition. Preference is given to establishing the molar $M_{2/n}O:SiO_2$ ratio in the synthesis gel composition in

10   the oxidic preparation method within a range from 0.01 to 0.045. The molar $SiO_2:Al_2O_3$ ratio in the synthesis gel composition is preferably established within the range from 50 to 150.

15   The synthesis gel composition is stirred until a homogen-eous gel is obtained. The crystallization is subsequently carried out under hydrothermal conditions, i.e. at a temperature of more than 100°C and a pressure of more than 1 bar. To this end, the synthesis gel is stirred in a

20   suitable pressure vessel. The crystallization is carried out preferably at temperatures of from about 120 to 200°C, especially preferably from about 140 to 180°C. The crystal-lization is particularly suitably carried out at a temperature of about 160°C. The crystallization time is

25   preferably from about 50 to 500 h, in particular from about 100 to 250 h. The crystallization time is influenced, for example, by the crystallization temperature. Under these synthesis conditions, a solid is obtained which has primary crystals having a mean primary crystal size of not more

30   than about 0.1 µm.

The crystallized product is subsequently removed from the mother liquor. To this end, the reaction mixture can be filtered, for example, with the aid of a membrane filter

35   press. However, other processes for removing the solid may likewise be carried out. A removal may, for example, also be effected by centrifugation. The removed solid is

subsequently washed with demineralized water. The washing
operation is preferably carried out until the electrical
conductivity of the washing water has fallen below
100 µS/cm.

The removed solid is subsequently dried. The drying is
carried out, for example, under air in customary drying
apparatus. The drying temperature is selected, for example,
within the range from 100°C to 120°C. The drying time is
generally in the range from about 10 to 20 h. The drying
time is dependent upon the moisture content of the removed
solid and on the size of the batch. The dried solid may
subsequently be comminuted in a customary manner, in
particular granulated or ground.

To remove the template, the solid may be calcined. The
calcination is carried out with ingress of air, the
temperatures selected being within the range from 400 to
700°C, preferably from 500 to 600°C. The time for the
calcination is generally selected to be between 3 and 12 h,
preferably 3 and 6 h. The times for the calcination relate
to the time for which the zeolite is kept at the maximum
temperature. Heating and cooling times are not taken into
account.

The content in the catalyst of exchangeable cations,
especially alkali metal ions, may be influenced, for
example, by treatment with suitable cation sources such as
ammonium ions, metal ions, oxonium ions and mixtures
thereof, and the exchangeable ions, especially alkali metal
ions, present in the inventive zeolite of the ZSM-12 type
may be exchanged. The catalyst laden with the corresponding
ions may subsequently be washed again and dried. The drying
is carried out, for example, at temperatures of from 110 to
130°C for a time of from 12 to 16 h. In order to convert
the catalyst into an acid-activated form in the event of an
exchange for ammonium ions, the catalyst may also be

calcined, for which, for example, temperatures in the range
of from 460 to 500°C can be employed for a period of from 6
to 10 h. Finally, the catalyst may also be ground.

5   The catalyst may be used in powder form. However, the
catalyst is preferably processed to moldings in order to
increase the mechanical stability and for better handling.
To this end, the inventive zeolite of the ZSM-12 type, as
detailed above, may, for example, be pressed to corres-
10   ponding moldings with or without addition of binders.
However, the shaping may also be effected by other proces-
ses, for example by extrusion. In this case, the resulting
powder is shaped after addition of a binder, for example
pseudoboehmite, to moldings. The moldings may subsequently
15   be dried, for example at temperatures of from 100 to 130°C.
Optionally, the moldings may also be calcined, for which
temperatures in the range from 400 to 600°C are generally
used.

20   Especially in the case of use for hydrogenations, dehydro-
genations and hydroisomerizations, the catalyst is also
covered with suitable activating compounds (active compo-
nents). The active components can be added in any way
familiar to those skilled in the art, for example by
25   intensive mixing, vapor deposition, saturation or impregna-
tion with a solution, or incorporation into the zeolite.
Preference is given to covering the catalyst with at least
one transition group metal, especially preferably with at
least one noble metal. To this end, the catalyst is
30   impregnated, for example, with a corresponding solution of
a transition group metal or of a noble metal. For the
coverage with platinum, a suitable example is an aqueous
H_2PtCl_6 solution. The impregnation solution is preferably
adjusted in such a way that the impregnation solution is
35   taken up fully by the catalyst. The catalysts are subse-
quently dried, for example, at temperatures of from about
110 to 130°C for from 12 to 20 h and calcinated, for

example, at from 400 to 500°C for from 3 to 7 h.

The inventive catalyst is suitable in particular for a
modification of hydrocarbons. For instance, the inventive
5   catalyst is suitable for reforming cuts from mineral oil
distillation, for increasing the flowability of gas oils,
for isomerizing olefins or aromatic compounds, for cataly-
tic or hydrogenating cracking and also for oligomerization
or polymerization of olefinic or acetylenic hydrocarbons.
10   Further applications are alkylation reactions, transalkyla-
tion, isomerization or disproportionation of aromatics and
alkyl-substituted aromatics, dehydrogenation and hydrogena-
tion, hydration and dehydration, alkylation and isomeriza-
tion of olefins, desulfuration, conversion of alcohols and
15   ethers to hydrocarbons and conversion of paraffins or
olefins to aromatics. In particular, the catalyst is also
suitable for isomerization and hydroisomerization of
naphthenes. The invention therefore also provides for the
use of the above-described catalyst for the conversion of
20   organic compounds, especially hydrocarbons.

Particular preference is given to the hydroisomerization of
higher paraffins. Higher paraffins are understood to mean
saturated linear hydrocarbons having a carbon number of
25   more than 5 carbon atoms, in particular of at least 7
carbon atoms. In particular, the catalyst is suitable for
the hydroisomerization of n-octane.

The hydroisomerization is preferably carried out in the
30   presence of aromatics, in particular of benzene.

The hydroisomerization is carried out in the presence of
hydrogen, preferably at temperatures below 290°C, prefer-
ably at from about 230 to 260°C, in particular at about
35   250°C. The pressure is carried out in the hydroisomeriza-
tion preferably within a range of from 1 to 50 bar at a
liquid hourly space velocity (LHSV) of from about 0.1 to

10 l per hour of hydrocarbon fed or of the hydrocarbon-containing mixture per liter of catalyst.

The invention is illustrated in detail with reference to the examples which follow.

Example 1: Synthesis of ZSM-12 (inventive)

For the production of the ZSM-12 zeolite, a synthesis gel composition was prepared which had the following composition:

$$8.5952 \ H_2O : SiO_2 : 0.0099 \ Al_2O_3 : 0.0201 \ Na_2O : 0.1500 \ TEAOH$$

TEAOH = tetraethylammonium hydroxide

271.2 g of sodium aluminate and 99.1 g of NaOH were dissolved with stirring in 9498.3 g of an aqueous solution of tetraethylammonium hydroxide (35% by weight) and 15905.3 g of water. The solution was initially charged in a pressure vessel of capacity 40 l which was equipped with a stirrer. With vigorous stirring, 10 226.1 g of precipitated silica having a specific surface area of 170 m^2/g were added in small portions. A highly viscous gel was obtained which had a pH of 13.7 at 24.0°C. The pressure vessel was closed and the contents were heated to 163°C over 12 h and then kept at this temperature for a total reaction time of 155 h. In the pressure vessel, a pressure of 13 bar was established.

After 155 h had passed, the pressure vessel was cooled to room temperature. The solid product was removed from the mother liquor by filtration and subsequently washed with demineralized water until the conductivity of the washing water was below 100 µS/cm. The filtercake was dried at 120°C with ingress of air over 16 h and subsequently calcined with ingress of air. For the calcination, the

dried solid was heated initially to 120°C at a heating rate of 1 K/min and kept at this temperature for 3 h. Subsequently, the solid was heated to 550°C at a heating rate of 1 K/min and this temperature was maintained for 5 h.

5

The analysis by x-ray diffraction showed that ZSM-12 had formed. The scanning electron microscopy analysis showed agglomerates having a diameter of about 0.8 µm which had formed from small primary crystals, and the agglomerates

10   exhibited a broccoli-like structure.

Example 2: Ion exchange

920 g of the zeolite ZSM-12 obtained in Example 1 were

15   suspended in a solution of 349.60 g of NH_4NO_3 in 4250.40 g of demineralized water and stirred for 2 h. The solid was removed by filtration and the filtercake washed four times with 500 ml each time of demineralized water. Subsequently, the washed filtercake was slurried again in a fresh

20   solution of 349.60 g of NH_4NO_3 in 4250.40 g of demineralized water and stirred for 2 h. The solid was again removed by filtration and washed with demineralized water until the conductivity of the washing water had fallen below 100 µS/cm. The filtercake was subsequently

25   dried under air at 120°C over 14 h and then calcined under air. To this end, the washed and dried filtercake was heated to 480°C at a heating rate of 1°C/min and then kept at this temperature for 8 h.

30   Yield: 916.7 g.

The chemical and physical analysis gave the data reported in Table 1:

35   Table 1: Analysis of the inventive zeolite of the ZSM-12 type

Ignition loss	7.9% by wt.
Na[a]	27 ppm (wt.)
Al[a]	0.99% by wt.
Si[a]	47.1% by wt.
$n(SiO_2) / n(Al_2O_3)$	91
C[a]	163 ppm (wt.)
Fe[a]	239 ppm (wt.)
Spec. surface area[b]	415 m^2/g

[a]: based on the ZSM-12 ignited at 1000°C

[b]: BET surface area to DIN 66131

5 ## Example 3: Production of moldings by extrusion

330 g of the ZSM-12 zeolite obtained in the acidic form in Example 2 were mixed over 15 min in a kneader with 156.3 g of commercial pseudoboehmite as a binder with addition of

10 294 g of demineralized water, and processed to a plastic mass. The mass was kneaded for a further 10 min and then 21.0 g of mold release oil (steatite oil) were added. The mass was subsequently extruded to moldings (d = 1/16"). The moldings were dried under air at 120°C over 16 h and

15 subsequently calcined under air. To this end, the moldings were initially heated to 120°C at a heating rate of 1°C/min and kept at this temperature for 2 h. Subsequently, the temperature was increased to 550°C at a heating rate of 1°C/min and the moldings were kept at this temperature for

20 5 h. The moldings were cooled to room temperature and then comminuted to a mean size of 3 mm. The catalyst had the chemical and physical properties reported in Table 2:

Table 2: Properties of an extruded inventive zeolite of

25 the ZSM-12 type (binder: pseudoboehmite)

Binder	Al_2O
Binder content	25% by wt.

Ignition loss   8.8% by wt.

$Na^{a)}$ 17.4 ppm (wt.)

$C^{a)}$ 381 ppm (wt.)

Spec. surface area[b]   363 m^2/g

[a]: after ignition at 1000°C

[b]: BET surface area to DIN 66131

5   Example 4:

Production of moldings comprising a silicate binder

300 g of the ZSM-12 zeolite in the H^+ form obtained in Example 2 were mixed in a kneader with 473.7 g of colloidal

10   silica having a weight fraction of 25% silica and dried with cold air until a plastic mass formed. The plastic mass was kneaded for a further 10 min and then 6.0 g of methyl-cellulose were added. Subsequently, the mass was extruded (d = 1/16″). The extrudates were dried under air at 60°C

15   over 16 h and then calcined with ingress of air. To this end, the dried extrudates were heated initially at a heating rate of 1 K/min to 600°C and kept at this temperature for 5 h. The extrudates were subsequently comminuted to a granule having a mean length of 3 mm.

20

b) Ion exchange

349.5 g of the granulated extrudate obtained under a) were introduced into a sieve and the sieve was immersed into a

25   solution of 158.32 g of NH_4NO_3 in 2103.44 g of demineral-ized water. The granule was left in the solution at room temperature over 1.5 h, in the course of which the sieve was regularly removed briefly from the solution in order to improve the ion exchange. The granule was removed from the

30   NH_4NO_3 solution and washed with demineralized water until the conductivity of the washing water had fallen to below 50 µS/cm. The granule laden with ammonium ions was dried under air at 120°C over 16 h and subsequently calcined. For

the calcination, the dried granule was heated initially at a heating rate of 1 K/min to 600°C and kept at this temperature for 5 h.

The properties of the catalyst are summarized in Table 3:

Table 3: Properties of an extruded inventive catalyst of the ZSM-12 type (colloidal silica binder)

Binder	Silicon dioxide
Binder content	30% by wt.
Ignition loss[a]	5.1% by wt.
Na[b]	44 ± 10 ppm (wt.)
C[b]	100 ± 20 ppm (wt.)
Pore volume (Hg)[c]	0.38 cm^3/g
Spec. surface area[d]	345 m^2/g

[a]: 1000°C/3 h

[b]: uncalcined

[c]: Hg method to DIN 66133

[d]: BET surface area to DIN 66131; multipoint method (p/po = 0.004 - 0.14)/conditioning: 350°C/3h; under reduced pressure

Example 5 (Comparative example):

Example 1 was repeated, except that colloidal silica was used instead of precipitated silica. The synthesis gel composition was selected as follows:

8.5952 H_2O : SiO_2 : 0.0099 Al_2O_3 : 0.0201 Na_2O : 0.1500 TEAOH

A solid was obtained which, in addition to ZSM-12 zeolite, contained ZSM-5 zeolite in a content of 30%. The solid was analyzed by scanning electron microscopy. From the scanning electron micrographs, the average diameter of the ZSM-12 primary crystals was determined to be 50-70 nm. The primary

crystals formed by combination of tightly packed, continu-
ous agglomerates. The proportion of the continuous
agglomerates in the total number of agglomerates was more
than 20%.

Example 6 (Comparative example):

A ZSM-12 zeolite, as described by S. Ernst, P.A. Jacobs,
J.A. Martens, J. Weitkamp; Zeolites, 1987, Vol. 7, 458-62,
was produced. The zeolite was produced using methyltri-
ethylammonium bromide (MTEABr). The zeolite powder had an
SiO_2/Al_2O_3 ratio of 108. Scanning electron micrographs under
1980- to 20 000-fold magnification showed rice grain-shaped
crystals having an average length of from 0.5 to 13 μm.

As described in Example 2, the zeolite powder was converted
to the acidic H^+ form by ion exchange with NH_4NO_3 and
subsequent calcination.

Example 7: Production of catalysts laden with platinum

The zeolites in the H form obtained in Examples 2 and 6
were each pressed to tablets without further additives with
the aid of a Carver laboratory press at a pressure of 18
tonnes. These tablets were crushed and the granules of
sieve fraction 0.5-1.0 mm were removed. These granules were
covered with 0.5% by weight of platinum by impregnating
with 30% H_2PtCl_6 solution. The granule was subsequently
dried at 120°C for 16 h and then calcined at 450°C for 5 h.
The properties of the granules are compiled in Table 4.

Table 4: Properties of an inventive catalyst of the ZSM-12
type laden with platinum

Zeolite	Example 2	Example 6
Shape	Granule, 0.5-1.0 mm	Granule, 0.5-1.0 mm
Hg[c)] pore volume; cm^3/g	0.50	0.49
Pore size distribution		
> 1750 nm (% by vol.)	2.21	5.26
1750-80 nm (% by vol.)	51.82	87.56
80-14 nm (% by vol.)	29.00	5.51
14-7.5 nm (% by vol.)	16.97	1.67
Spec. surface area[a)] (m^2/g)	401	281

[a)]: BET surface area to DIN 66131; multipoint method (p/po = 0.004-0.14)/conditioning: 350°C/3h; under reduced pressure

[c)]: HG method to DIN 66133

Example 8: Isomerization

The platinum catalysts obtained according to Example 7 were tested in a microreactor with pure n-heptane. The test conditions were as follows:

Reactor diameter:	8 mm
Catalyst weight:	2.0 g
Catalyst size:	sieve fraction of the granulated material of from 0.5 to 1.0 mm
Pressure:	20 bar
Temperature:	250°C
WHSV:	2.18 h^{-1}
H_2: n-heptane (molar):	1.3:1

The reactor was started up as follows: First, air was introduced at atmospheric pressure at a rate of 33.33 ml/min, and then the reactor was heated from room temperature to 400°C. This temperature was maintained for 1 h and then the temperature was lowered from 400°C to

250°C. The air stream was then interrupted and replaced by a nitrogen stream (33.33 ml/min) for 30 min. The nitrogen stream was finally replaced by a hydrogen stream (33.33 ml/min) for 30 min. The pressure was then increased

5   to 20 bar of H_2, and then pure n-heptane was introduced and the product stream was analyzed by gas chromatography. The peak areas of all C1 to C7 components were measured every 30 min. The peak areas of all i(so)-heptanes (e.g. methyl-hexanes, dimethylpentanes, etc.) were combined and denoted

10   as i(so)-heptane areas. The parameters are defined as follows:

Conversion (%)   = (1 − area (n-heptane)/total area) x 100
Selectivity (%)   = (area(i-heptane)/total area −
                    area(n-heptane)) x 100
Yield (%)   = (area (i-heptane)/total area) x 100

The inventive catalyst exhibited steady state conversion

15   and yield of 40% at virtually 100% selectivity. Cracking of the n-heptane to smaller molecules only took place in small fractions. The comparative catalyst exhibits no significant conversion of n-heptane at 250°C. The inventive catalyst exhibits a higher activity and converts n-heptane with very

20   high selectivity even at low temperatures.

Example 9:

Example 1 was repeated, except that the composition of the

25   synthesis gel was adjusted to the following ratio:

7.8918 H_2O : SiO_2 : 0.0091 Al_2O_3 : 0.0185 Na_2O : 0.1377 TEAOH

The crystallization time was increased to 175 hours.

30   Otherwise, the process procedure corresponded to the sequence described in Example 1. A crystalline solid was obtained which was composed of ZSM-12. The solid was analyzed by scanning electron microscopy. The scanning

electron micrograph reveals agglomerates which have a broccoli-like structure (open agglomerates). The proportion of closed agglomerates in the total number of agglomerates is less than 10%, while the open agglomerates correspond to
5   a proportion of more than 90%.

Example 10:

The platinum catalysts obtained according to Example 7 were
10   tested in a microreactor with pure n-octane. The test conditions were as follows:

Reactor diameter:	8 mm
Catalyst weight:	2.0 g
Catalyst size:	sieve fraction of the granulated material of from 0.5 to 1.0 mm
Pressure:	20 bar
Temperature:	245-250°C
WHSV:	2.25 h^{-1}
Molar H$_2$: n-heptane ratio:	1.3:1

The reactor was started up as follows: First, air was
15   introduced at atmospheric pressure at a rate of 33.33 ml/min, and then the reactor was heated from room temperature to 400°C. This temperature was maintained for 1 h and then the temperature was lowered from 400°C to 250°C. The air stream was then interrupted and replaced by
20   a nitrogen stream (33.33 ml/min) for 30 min. The nitrogen stream was subsequently replaced by a hydrogen stream (33.33 ml/min) for 30 min. The pressure was then increased to 20 bar of H$_2$, and then pure n-octane was introduced and the product stream was analyzed by gas chromatography.
25

In this test, the peak areas of all C1 to C8 components were determined every 30 min. The peak areas of all iso-octanes (e.g. methylheptanes, dimethylhexanes …) were com-

bined and denoted as isooctane areas. The parameters are defined as follows:

Conversion (%)   = (1 - area (n-octane)/total area) x 100
Selectivity (%)   = (area(isooctane)/total area -
                      area(n-octane)) x 100
Yield   = (area (isooctane)/total area) x 100

5 The catalyst was tested in the microreactor for 110 hours, in the course of which the activity and the selectivity were determined at 245 and 250°C.

10 The inventive catalyst (Example 7 in conjunction with Example 2) showed an extremely high conversion rate of more than 85% and a selectivity after 10 hours of 80% at 250°C. At 245°C, the conversion was 70% and the selectivity 85%.

15 In contrast, the comparative catalyst (Example 7 in conjunction with Example 6) exhibited a considerably lower selectivity and conversion rate. A comparative catalyst produced according to Smirniotis, J. of Catalysis 182, 400-416 (1999) had a very low conversion rate on the corresponding conditions. Only at higher temperatures of about 20 290°C was an acceptable conversion rate and selectivity observed.

Example 11

25 The solids obtained in Examples 1, 5 and 9 were analyzed for their specific volume by mercury porosimetry to DIN 66133. The experimental conditions were as follows:

Instrument   Porosimeter 4000; Carlo Erba, IT
Sample preparation   30 min under reduced pressure at
                        room temperature
Maximum pressure   4000 bar
Contact angle   141.3°

Hg surface tension   480 dyn/cm

The values found for the samples are listed in Table 5.

Table 5: Specific volume of zeolites calcined according to
Example 1, measured by mercury porosimetry

Pore radius range (nm)	Use of colloidal silica (Ex. 5)		Use of precipitated silica (Ex. 9)		Use of precipitated silica (Ex. 1)	
	rel.% by vol.	mm³/g spec.vol.	rel.% by vol.	mm³/g spec.vol.	rel.% by vol.	mm³/g spec.vol.
1.9 - 10	5.5	27	14	141	17	139
4 - 10	0.5	2.5	12	121	14	115
10 - 100	8.3	41	40	403	36	295
100 - 200	32	158	22	221	22	180
200 - 1000	46	226	14	141	16	131
1000 - 7500	8.2	40	10	101	9	74
Total	100	492	100	1007	100	819

The loose structure and thus the high fraction of cavities
between the primary crystals is shown in the mercury
porosimetry in the range of pore radii of from 1.9 to
100 nm. The calcined inventive zeolite from Examples 1 and
9 exhibits a specific volume of from about 110 to 125 mm³/g
in mercury porosimetry in the range from 4 to 10 nm. The
calcined comparative example (ZSM-12 zeolite, produced
using colloidal silica, Example 5) has a specific volume of
2.5 mm³/g in the range from 4 to 10 nm. In the range from
10 to 100 nm, the inventive zeolites of Examples 1 and 9
have a specific volume of from 300 to 400 mm³/g. The
zeolite from Example 5, employed for comparison, exhibits a
specific volume of 41 mm³/g in the range from 10 to 100 nm.

Example 12

The zeolites obtained in Examples 1, 5 and 9 were analyzed
for their pore radius distribution by nitrogen porosimetry

to DIN 66134. The experimental conditions were selected as follows according to the manufacturer's instructions and the evaluation was carried out by the method of "Dollim./Heal".

Instrument   Sorptomatic 1900; Carlo Erba, IT
Sample preparation   16 h/250°C/reduced pressure

The values found for the samples are reported in Table 6.

Table 6: Specific volume of zeolites calcined according to Example 1, determined by nitrogen porosimetry (cf. above)

	Use of colloidal silica (Ex. 5)		Use of precipitated silica (Ex. 9)		Use of precipitated silica (Ex. 1)	
Specific surface area m^2/g	418.37		393.59		439.00	
Pore-specific volume cm^3/g at p/p_0 = 0.9999	0.2176		0.5614		0.4758	
Pore radius range	spec.vol/ radius range	fraction in the volume	spec.vol/ radius range	fraction in the volume	spec.vol/ radius range	fraction in the volume
10 - 30 Å	0.045 cm^3/g	76%	0.031 cm^3/g	13%	0.045 cm^3/g	20%
30 - 200 Å	0.014 cm^3/g	24%	0.211 cm^3/g	87%	0.185 cm^3/g	80%
Total	0.059 cm^3/g	100%	0.242 cm^3/g	100%	0.230 cm^3/g	100%

Nitrogen porosimetry in the 10-200 Å range clearly shows the differences in the two structures. In the region of very small pores having a pore radius in the range of 10 - 30 Å, which are characteristic of compact-structure agglomerates, both the inventive zeolite (Examples 1 and 9) and the zeolite from Example 5 employed as a comparison have a volume of about 0.04 cm^3/g. However, the inventive

zeolite has in this range only approx. 15% of the total volume for the range of 10-200 Å under consideration, while the volume of 0.04 cm^3/g in this range for Example 5 corresponds to a fraction of the total pore volume (10-

5   200 Å) of 76%. In agreement with the mercury porosimetry, the differences between the inventive zeolite (Examples 1 and 9) and Example 5 become clear in the pore radius range of 30-200 Å in particular. In nitrogen porosimetry in the range of 30-200 Å, the calcined inventive zeolite exhibits

10   a specific volume in the range of about 0.18-0.21 cm^3/g. In the Example 5 employed as a comparison, a specific volume of only 0.014 cm^3/g was found in this range, which means that the zeolite for Example 5 exhibits a distinctly smaller fraction of cavities between the primary crystals.

15